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Technical Report Summary

A program has been developed to use spectroscopic insight and laboratory experiments to identify potentially important new laser candidiates.

Our group has discovered an innovative series of visible and ultraviolet lasers on high temperature diatomic molecules. To date both $S_2^{\uparrow}$ and $Te_2^{\uparrow}$ have been demonstrated to lase . Because of unique features of the diatomic molecular states, these molecules have potential to make highly efficient laser devices for DoD applications.

In particular, $S_2^{\uparrow}$ has numerous strong lasing transitions in the blue-green region of the spectrum for ONR applications, and many other laser lines in both the ultraviolet and red. The $S_2^{\uparrow}$ laser lases to high vibrational levels in the ground state. These levels are not populated at the 600°C necessary to form the dimers. Thus direct excitation schemes can produce very efficient conversion of energy to laser output.

The $S_2^{\uparrow}$ laser is able to withstand high power densities without degradation. It has all the usual desirable properties of gaseous systems for high average power and repetition rate. In addition the output will be line tunable over broad wavelength ranges. Collisions with rare gases serve to relax excited levels, but not quench the $S_2^{\uparrow}$.

Many other laser-suitable molecular species have been identified as well, by noting the desirable spectroscopic features of the $S_2^{\uparrow}$ molecule. Te_2 has already been shown to lase with the same efficacy as $S_2^{\uparrow}$. Other candidates just within group VI elements include SO, $Se_2^{\uparrow}$, TeS, TeO, TeSe, and SeS.

Technical Report

Enclosed is a reprint describing the technical details of the S_2 laser. Lasing action has been observed from Te_2 by optical pumping with a dye laser from 460-510 nm. The Te_2 lasing output has spanned the range of 565-620 nm.

Future Discharge Studies

The $S_2(B^3\Sigma_u^- - X^3\Sigma_g^-)$ laser transition has been observed by optical pumping with a frequency doubled dye laser. Hundreds of laser lines have already been seen from 360 nm to 630 nm, with the realistic potential for lasing on over ten thousand lines. With consideration of the numerous sulfur isotopes available, lasing action of the S_2 molecule may eventually encompass a nearly continuous line-by-line range from 330 nm to 700 nm. There will be numerous applications to DoD agencies if practical S_2 laser devices can be developed.

As a step forward in this direction, we are considering the possibility for direct electric discharge pumping of the S2 molecular laser. The S_2 molecule has fortuitous placement of its potential surfaces, which allow population inversions to be achieved readily. By close analogy to the data available for electron collisions with O_2, it is likely that electron collisions with S_2 will produce significant excitation on the $B^3\Sigma_u^- - X^3\Sigma_g^-$ transition. As observed in the optically pumped laser, small fractional populations produced in the $B^3\Sigma_u^-$ excited state will be inverted with respect to the high vibrational levels of the ground $^3\Sigma_g^-$ state. The exceptionally high gain of the S_2 stimulated emission makes the prospect for attaining laser action by direct electron excitation very favorable. Such a device, if successful, would lase on thousands of lines simultaneously, and would have a large number of potential applications.

In consultation with Richard T. Weppner at the Joint Institute for Laboratory Astrophysics, a number of designs for direct electron excitation of the S_2 laser have been considered. A design is necessary which pushes the current state of sophisticated technology to a maximum. The S_2 molecules must be contained in a 600^0C, meter-long tube, with long electrodes to produce a very fast ($\sim$10 nsec risetime), 20 kV discharge uniformly over it entire

length. The difficulties in developing such a discharge device for high temperature gas species has been a serious stumbling block for many investigators. Once developed, it would allow the study of laser action in many other high temperature vapor systems as well. The successful construction and operation of such a device would be regarded as a major step forward in our capability to study laser candidates which require high temperatures and fast discharge excitation.

Prospects for Successful Discharge Pumping of the Molecular S_2 Laser

A brief discussion of the parameters relevant to discharge excitation of the S_2 molecule should be considered. From spectroscopic measurements, values for the transition strengths of various S_2 lines have been given. More recent measurements of the $S_2(B^3\Sigma_u^-)$ lifetime give 45 nsec. Taking $A_{V''J''}^{V'J'}$ for a single line to be 1×10^6 sec^{-1}, we can obtain a coefficient for stimulated emission. For a single S_2 emission line at line center, λ = 500 nm, Doppler width = 0.054 cm^{-1} and T = 600°C, the stimulated emission coefficient is 1.5×10^3 cm^{-1} $torr^{-1}$ ($\sigma = 4.6\times10^{-14}$ cm^2). The density of S_2 molecules in a single vibration-rotation level of the $B^3\Sigma_u^-$ state needed to achieve a gain of e^5 in a 100 cm path length is conservatively estimated to be 1×10^{12}/cc. This number agrees well with what is observed empirically in our optical pumping experiments. Because the S_2 system is intrinsically high gain, stimulated emission can be achieved in a small number of passes. The short spontaneous lifetime (45 nsec) favors the use of fast electrical discharges initially. There is no reason to preclude that longer current pulses cannot be used later. Indeed, our optical pumping experiments have produced stimulated emission over the full duration of the 2 μsec pumping pulses. A gain of e^5 in a 1 meter path length will require only 4-5 transits for full laser action to be achieved. This is a conservative requirement for current pulses

in the initial range of 20-50 nsec duration and optical cavities of 1.5 meter path length.

On electron bombardment, excitation to the $^3\Sigma_u^-$ level will lead to a distribution of vibration-rotation states. If we neglect the weaker triplet splittings and recognize that only even rotational levels are allowed in the $^3\Sigma_u^-$ state,[5] there will be approximately 500 levels available at 600°C (V' = 0-9, J' = 0,2,4...100). We expect that an excited state density of approximately 5×10^{14}/cc distributed among all levels is adequate to produce laser stimulated emission. A density of 5×10^{14}/cc excited molecules is an entirely reasonable expectation for discharge excited lasers. Reasonable starting densities from discharge considerations will be in the range of 5×10^{16} to 5×10^{18} S_2 molecules/cc. If we choose 5×10^{17}/cc, then an excitation of only 0.1% of the ground molecules to the $B^3\Sigma_u^-$ state is required.

Under the condition where there are few collisions during the excitation pulse, the S_2 molecule will lase on thousands of lines simultaneously. In our optical pumping experiments, as many as 10-12 doublets lase simultaneously when exciting only a single level. In the electric discharge laser, a distribution of perhaps as many as 500 levels in the $B^3\Sigma_u^-$ state will lase. Data is available which indicates that rare gases can collisionally relax the vibration and rotation states of $S_2(B^3\Sigma_u^-)$ without quenching. By addition of He or Ar it is expected that this large number of excited states can be compressed into a few of the lowest vibrational levels. This is precisely the situation which occurs in the rare gas halide excimer lasers, XeF, KrF, etc. and in the recently discovered Hg Cl laser, where lasing is observed only from the lowest vibrational levels of the excited state. By standard techniques, wavelength selection and tuning of the laser output is readily

achieved. Using rare gases to produce rapid rotational and vibrational relaxation, significant fractions of the total available energy can be extracted on single frequencies. In addition, relaxation of lower laser levels is important to prevent the problem of bottlenecking and premature termination of the laser.

Electrons with energies in the range of 4-5 eV are expected to excite the S_2 ($B^3\Sigma_u^- - X^3\Sigma_g^-$) transition. From close analogy to the O_2 system, excitation of this transition can be made a dominant fraction of the total cross section at appropriate values of E/N (V/cm-torr). Electron excitation of the S_2 molecules to high vibrational levels of the ground state will have very small cross sections, and thus for lower laser levels above V" = 15 there is no appreciable excitation by either electron collisions or the 600°C temperature.

The prospects for direct electric discharge lasing in S_2 look very good, although there are always unforeseen difficulties. It is not possible to say at this time whether discharge problems will be encountered because of higher sulfur species such as S_3, S_4, S_5 . . . These are present to a small extent in the density and temperature ranges contemplated. Discharge characteristics in S_2 can be tested on the apparatus of Gallagher at JILA. Severe nonuniformities encountered in the discharge may often be eliminated by selective addition of other gases or by preionization techniques. Addition of other gases may be required also to modify the E/N to achieve more appropriate electron temperatures. The value of E/N must be high enough to produce primarily B-X excitation, but not too high, in order to prevent ionization of the S_2 molecules. Fluorescence from the $S_2(B^3\Sigma_u^-)$ can be monitored to optimize the discharge parameters before actual lasing is attempted.

Laser Design Considerations

The laser device contemplated embodies an extremely flexible design which will allow the major temperature and discharge parameters to be achieved with the capability for complete disassembly, cleaning, change of electrode profiles, change of electrode spacing, etc. Solving the extremely difficult design criteria problems is as crucial to the success of the project as are the basic scientific considerations. Credit for this design goes primarily to Richard T. Weppner.

In order to produce low inductance, 20 kV discharges across a 1 meter long tube which is heated to 600°C, a number of difficult problems must be overcome. A few might be mentioned. Special sealant techniques must be used to join metal electrodes into an electrical insulator tube. The entire tube, including windows, must be heated uniformly to prevent deposition of solid sulfur. Prevention of external arcing of the high voltage is a major concern. Problems with differences in coefficients of expansion of materials must be eliminated. The inductance of the discharge geometry must be kept extremely low to produce the short 20-50 nsec current pulses.

The device that has evolved in the minds of Richard Weppner and the principal investigator is shown in the viewgraph. The basic configuration is either a Blumlein laser circuit utilizing flat parallel plate transmission lines to generate the short electrical pulses, or a parallel cable design, which is also common for short pulsed nitrogen lasers. The major innovation is the capability to heat the laser tube to produce the desired high temperature species.

The main laser tube is 2" diameter Coors polycrystalline alumina (Al_2O_3 - AD998) ceramic material. The laser tube is precision ground flat on the ends. A groove is ground into each end to accommodate a Kovar split

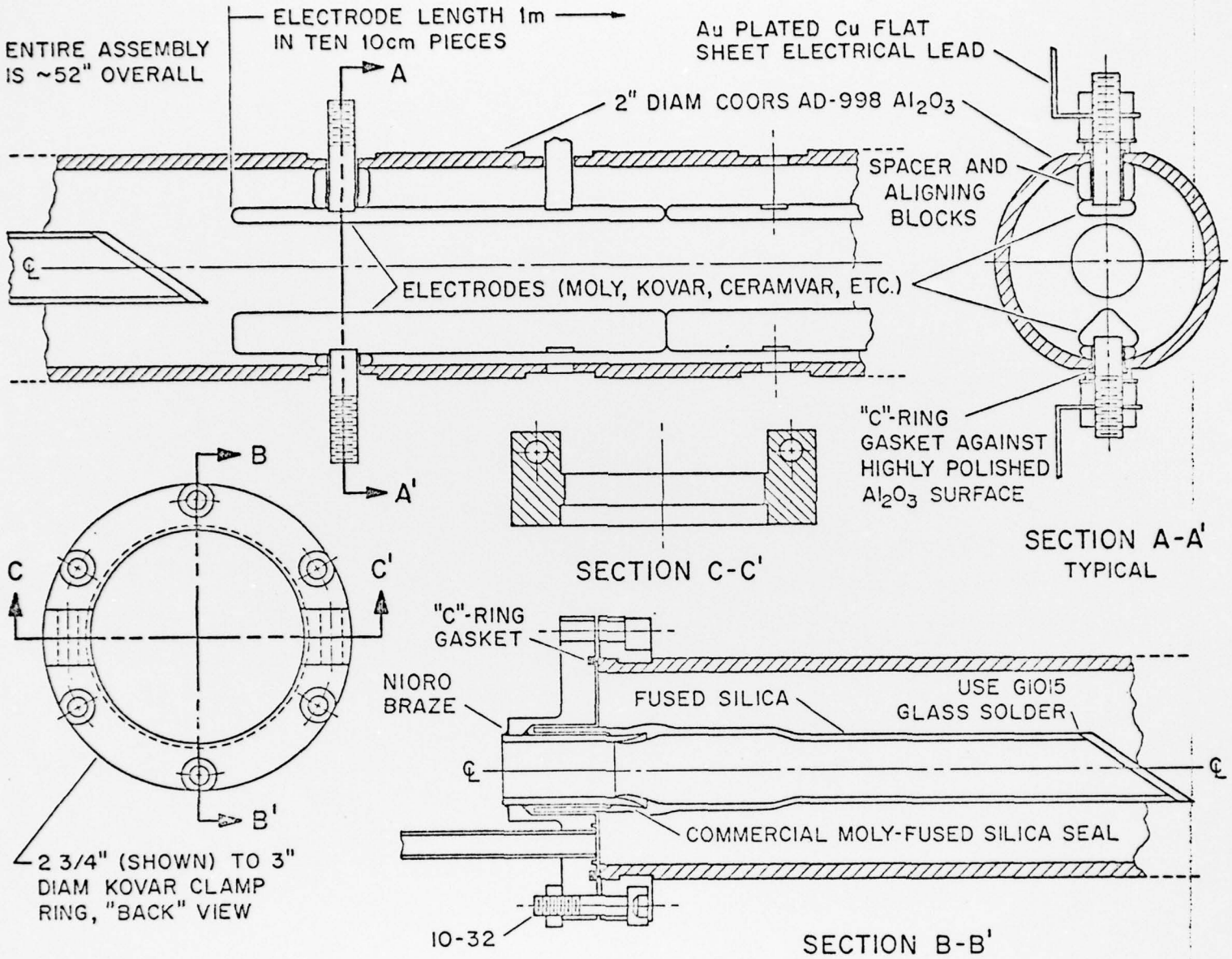
base flange, which holds on the window assemblies. The window flange assemblies are bolted to the split base flange, with vacuum seal provided by compression of a metal "c" ring. These "c" ring vacuum seals withstand temperatures higher than will be encountered in heating the main body of the tube to 600°C.

The window assemblies start from a Kovar flange. A molybdenum tube is brazed to the Kovar flange with a nickel-gold alloy, and a quartz-to-molybdenum seal provides the final transition to the actual quartz Brewster window. The Brewster window is sealed to the quartz tubing with a solder glass technique. These solder glass seals have proved to be a superior method of fusing laser quality quartz Brewster windows to quartz tubes for high temperature operation in our optically pumped S_2 laser. No loss in optical quality of the window is seen. The whole window assembly is capable of withstanding over 400°C, well above the temperature required to prevent deposition of sulfur. The main body of the laser tube will be heated to over 600°C, the temperature necessary to generate primarily sulfur dimers at the densities anticipated. Each window assembly will have a 1/4" tube welded into the kovar flange for evacuation and introduction of gases, and for control of the vapor pressure of sulfur at lower temperatures, 180-300°C.

Electrodes made of molybdenum or another suitable material are inserted the length of the Coors ceramic tube. By making each electrode in 10 sections, 10 cm long, problems caused by differing thermal expansion coefficients are minimized. Each electrode will be held by two studs, and only a small, 0.005", expansion difference is expected between the electrode material and the ceramic tube over the 5 cm stud spacing. When heated to operating temperature, the electrode sections will nearly contact each other on their ends. All electrode surfaces are carefully polished and rounded to minimize

filamentary arc formation in the gas discharge. Each electrode section is carefully centered and aligned by properly rounded spacers, and the vacuum seals made under the bolt heads by compression of metal "c" rings. Precision ground flats are needed at each point in the ceramic tube where "c" ring seals are made. Electrical contact is made from the parallel plate capacitors or from the parallel cables to each of the studs. Thus the current can be uniformly distributed over the entire 1 meter path length. Heaters are commercial half cylinders which are put together in sections and potted for further insulation. Great care must be taken to insulate the high voltage feeding to the electrode studs from the metal windings of the heaters. The resultant device will be capable of temperatures even higher than required for the first experiments on S_2. The versatility of the design and ability to make changes has been an important consideration. For example, through the window flanges, a preionization (corona wire) electrode can be added if necessary. Electrode spacing and geometries can be readily changed. We anticipate that the device will have tremendous potential, not only for the S_2 system, but for other metal vapor systems as well.

HIGH TEMPERATURE SPECIES ELECTRIC DISCHARGE LASER



A tunable visible and ultraviolet laser on S_2 ($B^3\Sigma_u^- - X^3\Sigma_g^-$)

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Laser action has been achieved on the $B\,^3\Sigma_u^- - X\,^3\Sigma_g^-$ transition of S_2 by optical pumping with a frequency-doubled dye laser and a nitrogen laser. The observed lasing is line tunable from 365 to 570 nm. The S_2 molecule is a promising candidate for an efficient scalable ultraviolet laser system.

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There is widespread interest in the development of efficient tunable visible and ultraviolet lasers. We have achieved lasing in a promising new molecular system, the sulfur dimer, S_2, on its $B^3\Sigma_u^- - X^3\Sigma_g^-$ transition. Emission from the $S_2(B-X)$ is widely observed in flames, shock tubes, and discharges whenever compounds of sulfur are present.[1,2] In this first demonstration of the lasing characteristics of S_2, line tunable laser action is observed from 365 to 570 nm by pumping with a frequency-doubled dye laser. Initial results indicate that the S_2 system is capable of nondegradable operation, is scalable, has potential for efficient operation, and may offer promise for successful pumping by other excitation schemes.

A report of an S_2 laser on the $^1\Sigma_g^+ - {}^3\Sigma_g^-$ transition at 1.1 μm has been made.[3] The S_2 laser considered here lases on a different transition. Figure 1 sketches the approximate potential surfaces for the known S_2 molecular states.[4] Although many details about these surfaces and the exact locations of other states are not known, several qualitative features of these potential surfaces are most important. All of the lasing states explored in this study, including $v' = 2, 3, 4, 5, 6, 7$, are well below the dissociation limit of the S_2 molecule. Thus, the lowest vibrational levels of the $B^3\Sigma_u^-$ state, although heavily perturbed, are not predissociated.[5-8] The potential surfaces are fortuitously displaced so that the lowest vibrational levels of the $B^3\Sigma_u^-$ excited state are situated over high vibrational levels of the ground $X^3\Sigma_g^-$ state, which are not populated at the 500 °C operating temperature. The Franck-Condon factors for these $B-X$ transitions are as large as 0.1 for many bands and cover broad spectral ranges before diminishing.[9] The measured fluorescence lifetimes of individual states is approximately 20 nsec, giving $A_{v'J'}^{v''J''}$ coefficients for single lines on the order of 10^5-10^6 sec^{-1}.[9,10] Thus it is reasonable in the experiments described here that high gain laser action from a single rotational level in $v' = 5$ was observed on numerous lines over a 365–530-nm range. Taking into account that successive vibrational bands nearly overlap, and the availability of numerous sulfur isotopes, almost complete coverage of the ultraviolet and visible regions of the spectrum is possible.

The experimental setup for generating S_2 molecules consists of a 12-cm-long Brewster angle, all fused-quartz cell with a single sidearm. The cell is evacuated with a few milligrams of sulfur inside, sealed off, and housed in a 500 °C tube furnace. Such sealed-off cells have operated successfully without degradation for several months. The vapor pressure of sulfur inside the cell is adjusted between 1 and 10 Torr with the sidearm maintained independently at 180–240 °C. At temperatures above 500 °C and at these low vapor pressures, the large ring molecules of sulfur break down to give predominantly sulfur dimers.[11] Initial experiments were accomplished with a nitrogen laser pump (1–10 mJ per pulse, 10 nsec). The nitrogen laser, 337.1 nm, overlaps with the (2, 4) band of S_2.[12] The pump laser is focused through a partially transmitting input mirror longitudinally into the S_2 cell. The S_2 laser mirrors are typically 99%R and 50%R over the visible or ultraviolet range desired. At a pressure of ~10 Torr, bright spontaneous fluorescence from the side is visible, even with the room lights on, when the nitrogen laser excites the S_2. Stimulated emission was first observed in the blue region of the spectrum. Calculations made by analogy to other dimer systems suggested that high gain lasing

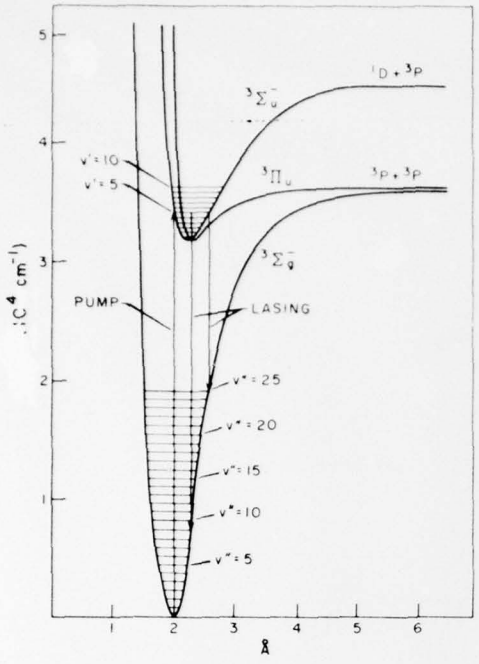

FIG. 1. Approximate known potential surfaces for the S_2 molecule (Ref. 4). The levels $v' \leq 9$ are bound, but often perturbed. They are characteristic strong emitters. The levels $v' \geq 10$ are not observed in emission, probably due to strong predissociation. One pump excitation line and the maximum and minimum observed lasing wavelengths are shown for $v' = 5$. Lasing transitions are also observed to almost all v'' levels in between, whenever the Franck-Condon factors are not nearly zero.

action on S_2 would be observed with this short pulse excitation.

In more recent and refined experiments, the S_2 laser was pumped in a similar fashion with a frequency-doubled dye laser. This provided the advantage of tuning the pump laser over a variety of bands absorbing from 290 to 305 nm. Transitions corresponding to (v', v'') from (3,0) to (7,0) were excited.[12] The dye laser has characteristic pulsed energies in the ultraviolet of 0.5 mJ, 2 μsec duration, and a 0.5-cm^{-1} bandwidth using a low-finesse (R = 30%) etalon. The peak power with the dye laser is considerably lower than for the nitrogen pump. Most stable lasing was achieved when the dye laser was focused to a beam radius of 100 μm in a few Torr of S_2.

All of the $^3\Sigma_u^-$ vibrational states which were excited by the doubled dye laser exhibited strong lasing action throughout the visible. The lasing wavelengths were primarily in the violet, blue, blue-green, and green regions, centered about the reflectivity maximum of the mirrors, 450–550 nm. The strongest observed laser lines correspond well with the wavelengths of emission bands recorded by Rosen[12] for each S_2 level pumped. Sharp P- and R-branch doublets are observed for each lasing transition. For a single pump wavelength, as many as eight to ten doublets, spaced by the vibrational levels in the ground state, lased simultaneously in the broad-band cavity. Lasing was observed both with and without narrowing of the pump bandwidth. More powerful and stable operation was achieved with modest narrowing from 5 to 0.5 cm^{-1}. Experimentally the pump energy needed for threshold in the S_2 laser with the 50% output coupler was 100 μJ. The 0.5-cm^{-1} pump spectrum however is ten times broader than individual S_2 lines, and much of the pump light was not being used to produce the lasing state. Gain was observed to be superfluorescent on the strongest lines at higher S_2 pressures. Transitions as short in wavelength as 400 nm and as long as 570 nm were observed to lase, where both mirrors had a reflectivity of only 50%. A cavity composed of R = 99% at 360–410 nm and R = 40% at 350–400 nm mirrors sustained stable and strong lasing at wavelengths observed from 365 to 390 nm. In this setup the strongest visible lines were not completely suppressed even though the effective reflectivity on each mirror was less than 20%. Energy conversion was measured to be 2% for the total visible output of the S_2 laser.

Each S_2 band is 15–25 Å wide in absorption, and tuning has been accomplished over entire bands. Typically there are strong S_2 absorption lines every few cm^{-1} in a single vibrational band. However, there are numerous rotational statellites and overlapping bands. In practice, three to four lasing absorptions are observed per cm^{-1}. In regions of the band heads, the spectrum is even more dense. The pump laser was tuned over numerous lines in the (5,0) band, and the lasing output tuned correspondingly within the (5,21) band which was observed in the monochromator. With the numerous isotopes of sulfur available, almost any desired wavelength can be attained.

From a number of standpoints, the optically pumped S_2 laser described here is not fully optimized. As mentioned, the pump spectrum is a factor of 10 times broader than the S_2 lines. Proper mode matching of the focused pump beam to the S_2 laser cavity has not been attempted. The present S_2 laser has 3-m–radius-of-curvature mirrors. This resonator sustains a beam area inside the cavity an order of magnitude larger than the pump zone. Bright spontaneous emission is observed from the side of the S_2 cell because of the short radiative lifetime. Even when the best lasing was obtained, this emission was not dramatically reduced in intensity. We anticipate that more proper mode matching will greatly enhance the output. In these first experiments, also, the laser gain length was restricted to the 12-cm cell. The laser operation was observed to fall off abruptly with increased pressure. Most likely S_2–S_2 collisions are quenching the $B^3\Sigma_u^-$ state. Operation with a longer path length and lower total S_2 pressure should greatly improve the conversion efficiency. Only lasing transitions which originate from states directly excited by the pump laser are observed. In the present laser, molecules which are vibrationally and rotationally relaxed cause excitation to be lost from the system for laser output. Experiments are in progress to test whether selective vibrational and rotational relaxation, by addition of other molecules or rare gases, can enhance the efficiency or tuning range without quenching. The S_2 laser pulse in our system follows precisely the entire time duration and shape of the 2-μsec doubled

dye laser pulse. However relaxation rates will be important to determine whether bottlenecks could occur in the ground-state lasing levels.

The sulfur laser compares very favorably to the other optically pumped molecular dimer systems, I_2,[13] Na_2,[14] and Br_2.[15] With fully optimized parameters, conversion efficiencies should far exceed the 2% measured here. It is likely that other pump sources such as the XeF laser or single-line high-power arc lamps[9] may be suitable to excite the S_2 molecule. Since strong S_2 $^3\Sigma_u^-$ emission has been observed under numerous other conditions, it is likely that chemical or electrical pumping schemes are possible also. The frequent occurrence with which sulfur dimers are observed to be formed in the appropriate excited state warrants further investigation of S_2 as an efficient and tunable visible and ultraviolet laser source.

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